Progress Report

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2. Project title: Reduced and validated kinetic mechanisms for hydrogen-CO-air combustion in gas turbines

3. Date of Report: March 31, 2006; Period covered: Jan.1-Mar. 31, 2006

4. Executive Summary

The high pressure spherical bomb was modified for syngas flame speed measurements. An accurate spectral dependent radiation model is developed for the modeling of radiation absorption of CO, H_2O, and CO_2 in syngas at high pressure. The results showed that radiation absorption of the emitting gases in hydrogen syngas significantly change the flame speed at high pressures.

5. Results

The results reported here were also reported in the report of second quarter (March 1 –June 30, 2006) [1]. This is because the PI did not know this project was funded until late February of 2006. We were not able to start the research until March 1, 2006. In addition, the graduate student was in final examination period and did not have time to start the work. Therefore, the project was delayed by two months. In March, the PI conducted a theoretic study of flame radiation for syngas combustion at high pressures and reported these results together with the experimental work in the second quarter report [1].

5.1 Preparation of syngas flame speed measurement using the high pressure spherical bomb

The dual chamber, high pressure spherical bomb was modified for flame speed measurement of syngas at high pressures. At high pressures, the energy requirement to initiate ignition increases. Therefore, we redesigned the ignition circuits to increase to ignition energy up to 1 J per electrical discharge. In addition, in order to monitor the pressure change during the flame speed measurement, we installed a pressure sensor for both inner and outer chambers.

5.2 Numerical algorithm for spectral radiation on flame speed

The strong spectral radiation absorption of H_2O, CO, CO_2 and the appearance of large amount of $H_2O/CO/CO_2$ in the syngas raises the following question: what is the role of $H_2O/CO/CO_2$ radiation in flame speed and flammability limit? This concern becomes more serious when the ambient pressure increases.

For combustion gas radiation properties, a number of databases have been compiled based on line-by-line (LBL) [2, 3], and narrow band [4-5] models, and global full-spectrum model [6, 7]. The LBL is accurate at low temperatures, but requires excessive CPU time and is not suitable for high temperature combustion gases because the high temperature vibration-rotation absorption bands are not included. For global models, the weighted-sum-of-grey-gases (WSGG) model [6] and the full-spectrum correlated-k methods [7] were developed. These models have excellent computation efficiency but less accurate than the band models and have difficulties treating non-gray boundaries. The statistical narrow-band (SNB) models [4] are favored. Recent CO_2 absorption experiment [7] showed that EM2C SNB model has an excellent accuracy up to 1300 K. In the SNB model for non-homogeneous mixtures, the ray tracing method [8] and the Curtis-Godson approximation were widely used [8, 9]. However, the ray tracing method is computationally inefficient, and the Curtis-Godson approximation is accurate only in the optically thick and thin limits.

Lacis et al. [10] developed a new category of the SNB based correlated-k method (SNBCK). By reordering the absorption coefficients in LBL into a monotonic k-distribution in a narrow spectral range, the model can produce exact results at a small computation cost [11]. For inhomogeneous media, it was shown that CK model gives much better results than the standard Curtis-Godson correlation. Furthermore, it allows the implementation of conventional discrete ordinate method (DOM) [12]. However, the inversion of CK model requires numerical iterations and sometimes convergence is not guaranteed. In addition, the SNB-CK model has not been considered in radiation modeling for spherical flames.

In this study, to resolve the convergence difficulty of SNB-CK in multi-component mixtures and to accelerate the computation efficiency, we developed a fitted SNB-CK model and extended it for radiation calculation of spherical flames. Hereafter, we call this model FSNB-CK.

In the SNB model, the gas transmissivity, τ_ν, at wave number ν over a light path L is given as [13]

$$\tau_\nu = \exp\left[-\pi b\left(\sqrt{1+4SL/\pi b}-1\right)/2\right] \tag{1}$$

where $b = 2\bar{\beta}_\nu/\pi$, $S = \bar{k}_\nu X p$, and $\bar{\beta}_\nu = 2\pi\bar{\gamma}_\nu/\bar{\delta}_\nu$ are the SNB model parameters [4] for CO, CO_2 and H_2O. The bandwidth is 25 cm^{-1} for wave numbers between 150 and 9300 cm^{-1}. By performing an inverse Laplace transformation, the distribution function of the absorption coefficient at each narrow band can be obtained as [10]

$$f(k) = 0.5k^{-3/2}(bS)^{1/2}\exp\left[0.25\pi b\left(2 - S/k - k/S\right)\right] \tag{2}$$

and the cumulative function of k-distribution

$$g(k) = \int_0^k f(k')dk' \tag{3}$$

can be given as

$$g(k) = \frac{1}{2}\left[1-\mathrm{erf}\left(\sqrt{\frac{\pi bS}{4k}} - \sqrt{\frac{\pi bk}{4S}}\right)\right] + \frac{1}{2}\left[1-\mathrm{erf}\left(\sqrt{\frac{\pi bS}{4k}} + \sqrt{\frac{\pi bk}{4S}}\right)\right]\exp(\pi b) \tag{4}$$

Using the cumulative distribution function, the average radiation intensity at each narrow band can be calculated using a Gauss type quadrature [11]

$$I_\nu = \sum_{i=1}^{N} \omega_i I_\nu [k_i(g_i)] \tag{5}$$

where N is the number of Gaussian quadrature points, ω_i the weight function, and g_i the Gaussian point. The estimation of $k_i(g_i)$ from Eq. 4 needs iterations and sometimes diverges for multi-component mixtures [10]. In order to resolve this problem, we rewrote Eq. 4 as

$$k_{ii}/S(b)=F_i(b),\ i=1,\ N \tag{6}$$

Here $F_i(b)$ is a fitted function at all Gaussian points for CO, CO_2 and H_2O using the SNB data [4], respectively. Therefore, Eq. 4 is replaced by Eq. 6 using 3×N fitted functions. Since a four-point Gaussian quadrature is accurate enough for Eq. 5, we only need 12 fitting functions. These fittings are straight forward and the maximum error between B=10^{-4} and 10^4 for k_i/S is less than 0.5%. For b<10^{-4} and b>10^4, the optically thin and thick limits can be applied. The use of Eq. 6 and high accuracy of fitting completely removed the need of iteration for $k_i(g_i)$ from Eq. 4 and thus this technique avoids the problem of divergence.

For radiating gas mixtures, the approximate treatment of overlapping bands from optically thin and thick limits [10-11] was employed

$$S = S_{CO} + S_{CO_2} + S_{H_2O},\quad S^2/b = S_{CO}{}^2/b_{CO} + S_{CO_2}{}^2/b_{CO_2} + S_{H_2O}{}^2/b_{H_2O} \tag{7}$$

The contribution from soot radiation at each narrow band can be added to the gas phase radiation. The spectral radiative transfer equation in spherical coordinates at each band in m direction is given as

$$\mu_m \frac{\partial I_{\nu m}}{\partial r} + \frac{2\mu_m I_{\nu m}}{r} + \frac{1}{r}\frac{\partial}{\partial \mu_m}[(1-\mu_m{}^2) I_{\nu m}] = -k_\nu I_{\nu m} - k_\nu I_{b\nu} \tag{8}$$

where μ_m=cos(θ_m), and m is the index from 1 to M of polar angle θ, and I_b the blackbody radiation intensity.

By using the following angular derivative,

$$\frac{\partial}{\partial \mu_m}[(1-\mu_m{}^2) I_{\nu m}] = \frac{\alpha_{m+1/2} I_{m+1/2} - \alpha_{m-1/2} I_{m-1/2}}{\omega_m}$$
$$\alpha_{m+1/2} - \alpha_{m-1/2} = -2\omega_m \mu_m,\ \alpha_{1/2} = \alpha_{M+1/2} = 0 \tag{9}$$

and the central difference scheme for spatial and angular discretizations,

$$2I^C_{i+1/2,m} = I_{i,m} + I_{i+1,m} = I^C_{i+1/2,m+1/2} + I^C_{i+1/2,m-1/2} \tag{10}$$

the final discretized radiation transfer equation for μ_m<0 becomes

$$2|\mu_m| \frac{I^C_{\nu,i+1/2,m} - I_{\nu,i+1,m}}{r_{i+1} - r_i} + \frac{(\alpha_{m+1/2} + \alpha_{m-1/2})(I^C_{\nu,i+1/2,m+1/2} - I^C_{\nu,i+1/2,m})}{r_{i+1/2}\omega_m} = k_\nu(-I_{\nu,i+1/2,m} + I_{b\nu,i+1/2}) \tag{11}$$

The boundary conditions at r = 0 and $r = r_2$ are given as

$$I_m = I_{M+1-m} \text{ at } r = 0; \quad I_m = \varepsilon_w I_{bw}(T_w) + (1-\varepsilon_w) \sum_{\mu_m > 0} I_m w_m \mu_m / \pi \text{ at } r = R \tag{12}$$

The total volumetric heat source term of radiation is given as

$$\dot{q}_r = \sum_{j=1}^{N-band} \Delta\nu \sum_{n=1}^{N} \omega_n k_n \left(\sum_{m=1}^{M} I_{j,n,m} - 4\pi I_{bj} \right) \tag{13}$$

The effects of spectral radiation absorption on the flame speed at normal and elevated pressures were experimentally and numerically investigated using the CO_2 diluted outwardly propagating CH_4-O_2-He flames. Experimentally, the laminar burning velocities of CH_4-O_2-He-CO_2 mixtures at both normal and elevated pressures (up to 5 atm) were measured by using a pressure-release type spherical bomb. The results showed that radiation absorption with CO_2 addition increases the flame speed and extends the flammability limit. In addition, it was also shown that the increase of pressure augments the effect of radiation absorption.

Previous analysis in [14] shows that radiation absorption has less effect as pressure increases because the total chemical heat release increases with the pressure. In order to examine the effect of pressure, the radiation absorption effect and comparison of different radiation model for CH_4+{$0.3O_2$+0.2He+$0.5CO_2$} mixtures at 2 atm is shown in **Fig. 1**. It is seen that radiation absorption render that optically thing model (OPTM) invalid.

In addition, the SNB gray model over-predicts the flam speed and burning limit. The present FSNB-CK model predicts much better flame speeds compared to the experimental data. In addition, by comparing the results with that at one atmosphere, it is seen that the radiation effect becomes much stronger at 2 atm. Different from the previous theory [14], the present result shows that radiation absorption increases with pressure. This is because an infinite optical thickness was assumed in the theory so that all the radiation heat loss from the burned zone will be absorbed by the unburned mixture. In the present experiment, the optical thickness is finite (about 1.0~6.0 estimated from OPTM) so that the increase of pressure enlarges the optical thickness and radiation absorption. Therefore, for syngas combustion with high CO and H2O concentrations, neither adiabatic nor optically thin radiation model can predict accurate flame speeds for the validation of kinetic model.

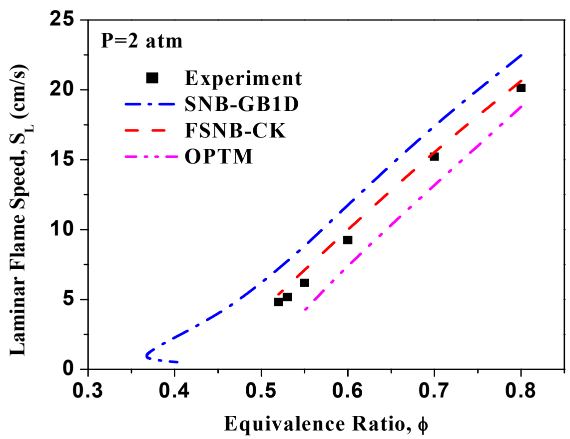

Fig.1 Measured and predicted laminar flame speeds of CH_4-{$0.3O_2$+0.2He+$0.5CO_2$} flames as a function of equivalence ratio at 2 atm.

5.3 Conclusions

The high pressure spherical bomb was modified for the flame speed measurement of syngas. A new fitted statistical narrow-band correlated-k (FSNB-CK) model was developed and validated for accurate radiation prediction in spherical geometry. The effects of spectral radiation absorption on the flame speed at normal and elevated pressures were experimentally and numerically investigated using the CO_2 diluted outwardly propagating CH_4-O_2-He flames. The results showed that radiation absorption with CO_2 addition increases the flame speed and extends the flammability limit. In addition, it was also shown that, unlike that conventional theory the increase of pressure augments the effect of radiation absorption. The present model not only performs better the SNB gray gas model and the optically thin model but also showed that prediction of flame speeds for combustion mixtures with high CO_2/CO/H_2O blending requires accurate radiation modeling. Neither adiabatic nor optically thin radiation models can provide kinetic validation at high pressure and near limit conditions.

5.5 References

1 Y. Ju and F. L. Dryer, Reduced and validated kinetic mechanisms for hydrogen-CO-air combustion in gas turbines, *DOE Progress Report*-DE-FG26-06NT42716, Mar.1-Jun.30, 2006

2. L.S. Rothman, C.P. Rinsland, A. Goldman, S.T. Massie, D.P. Edwards, J.M. Flaud, A. Perrin, C. Camy-Peyret, V. Dana, J.V. Mandin, J. Schroeder, A. McCann, R.R. Gamache, R.B. Wattson, K. Yoshino, K.V. Chance, K.W. Jucks, L.R. Brown, V. Nemtchinov, P. Varanasi, *J. of Quant. Spect. Radiative Transfer* 60 (1998) 665.
3. N. Jacquinet-Husson et al., *J. of Quant. Spect. Radiative Transfer* 62 (1999) 205.
4. A. Soufiani, J. Taine, *Intl. J. Heat Mass Transfer* 40 (1997) 987.
5. W.L. Grosshandler, Radical, *Int. J. Heat Mass Transfe*r 23 (1980) 1147.
6. M.K. Denison, B.W. Webb, *J. Heat Transfer* 117 (1995) 359.
7. M.F. Modest, H. Zhang, *J. Heat Transfer* 124 (2002) 30.
8. T.K. Kim, J.A. Menart, H. S. Lee, *J. Heat Transfer* 113 (1991) 946.
9. H. Bedir, J.S. Tien, H. S. Lee, *Combust. Theory Model.* 1 (1997) 395.
10. A.A. Lacis, V.A. Oinas, *J. Geophysical Res.* 96 (1991) 9027.
11. F. Liu, G.J. Smallwood, Ö.L. Gülder, *J. of Quant. Spect. Radiative Transfer* 68 (2001) 401.
12. W.A. Fiveland, *J. Heat Transfer* 106 (1984) 699.
13. D.B. Ludwig, W. Malkmus, J. E. Reardon, J. A. L. Thomson, NASA SP3080 (1973).
14. G. Joulin, B. Deshaies, *Combust. Sci. Tech*. 47(1986) 299.

6.0 Secrets and Classified data

The report included in Section 5 does not have any trade secrets and business sensitive data.

7.0 Status Reporting

7.1 Cost Status

Cost Plan/Status

Baseline Reporting Quarter	Year 1 Start: 2006.4.1 End: 2007.3				Year 2 Start: 2007.4 End: 2008.3				Year 3 Start: 2008.4 End: 2009.3			
	Q1	Q2	Q3	Q4	Q5	Q6	Q7	Q8	Q9	Q10	Q11	Q12
Baseline Cost Plan (SF-424A)												
Federal share												
Non-Federal Share												
Total Planned (Federal & Non-Federal)	$10,333											
Cumulative Baseline Cost	$10,333											
Actual Incurred Costs (SF-424A)												
Federal share												
Non-Federal Share												
Total Planned (Federal & Non-Federal)	$0											
Cumulative Baseline Cost	$0											
Variance												
Federal share												
Non-Federal Share												
Total Planned (Federal & Non-Federal)	$10,333											
Cumulative Baseline Cost	$10,333											

7.2 Milestone Status

(1) Project Milestones

In the planned milestones, the project starts from March 1st, 2006. Because the announcement of funding was Feb. 16, 2006 and that the first year graduate student course exams, we started the project from March 1st, 2006. This two month-delay will not significantly change the progress of the planned research.

(2) Actual Progress towards the Project Milestones

In this quarter, we We have modified the new high pressure chamber and measured the flame speeds of syngas mixtures up to 20 atm. We also developed a new modeling algorithm for accurate prediction of thermal radiation from H_2O, CO, and CO_2 in syngas.

Milestone Plan/Status Report

Task/ Subtask Number	Critical Path Project Milestone description	Project Duration Start: End:												Planned start Date	Planed End Date	Actual Start Date	Actual End Date	Comments (Notes, explanation of deviation from baseline plan)
		Project Year (PY) 1				Project Year (PY) 2				Project Year (PY) 3								
		Q 1	Q 2	Q 3	Q 4	Q 5	Q 6	Q 7	Q 8	Q 9	Q 10	Q 11	Q 12					
1.1		*												2006.1	2006.3	2006.3	2006.6	Announcement of grants was too late. Graduate student was for final exam.

8. Summary of Significant Achievements

The high pressure spherical bomb was modified for the flame speed measurement of syngas up to 20 atm. A new fitted statistical narrow-band correlated-k (FSNB-CK) model was developed and validated for accurate radiation prediction in spherical geometry. The results showed that radiation absorption with CO_2 addition increases the flame speed and extends the flammability limit. The present model not only performs better the SNB gray gas model and the optically thin model but also showed that prediction of flame speeds for combustion mixtures with high $CO_2/CO/H_2O$ blending requires accurate radiation modeling. Neither adiabatic nor optically thin radiation models can provide kinetic validation at high pressure and near limit conditions.

9. Actual Delays and Plans to Resolve Them

The project start was delayed by two month because of the first year graduate student final exams and the late announcement of research grant. This delay will be resolved during the graduate students and undergraduate students' summer research.

10. Products Produced during the Research Period